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(54) CHEMICAL NICKEL PLATING BATH AND PROCESS

(71) We, TEXAS INSTRUMENTS INCORPORATED, a Corporation organized according to the laws of the State of Delaware, United States of America, of 13500 North Central Expressway, Dallas, Texas, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention lies in the field of electroless nickel plating and more particularly relates to an improved electroless nickel plating bath and to a process of using the improved bath in plating the surface of various substrates.

Chemical nickel plating or electroless nickel plating, as it is known to the art, has been practiced for some years and is based upon the catalytic reduction of nickel ions by hypophosphite ions in the presence of water in accordance with the following equation:

$$Ni^{++} + 2(H_2PO_2)^{-} + 2H_2O \xrightarrow{\text{catalyst}} 2(HPO_3)^{-} + H_2 + Ni^{\circ}$$

Thus, the electroless nickel plating process involves the reduction of nickel ions and the catalytic oxidation of hypophosphite ions to the corresponding phosphites. In practice, using a conventional electroless nickel plating bath consisting of an aqueous solution of a soluble salt such as nickel sulfate hexahydrate and a soluble hypophosphite such as sodium hypophosphite monohydrate, the phosphite concentration resulting from the oxidation of the hypophosphite ions continues to build up until the threshold of nickel phosphite solubility is reached at which time precipitation will occur. This phenomenon has been a major problem in connection with the use of electroless nickel plating baths inasmuch as precipitation of nickel phosphite leads to spontaneous decomposition of the bath around the initially formed precipitate.

The use of various selected nickel complexing or chelating agents has been proposed as a means of minimizing or preventing the precipitation of nickel phosphite. However, the selection of suitable chelating agents has presented a difficult problem since the stability of the nickel complex formed must not be too great or too small if practical and effective control of nickel phosphite precipitation is to be achieved. On the one hand, if the nickel complex is too stable, little or no coating or deposition of nickel will occur. On the other hand, if the stability of the nickel complex is too weak, premature and undesired precipitation of nickel phosphite will still occur even at relatively low concentrations of hypophosphite ions. Many chelating agents, such as organic hydroxy acids, have been found unsatisfactory in practice because, when added to the bath, they unduly retard the deposition rate of nickel. For example, tartaric acid, malic acid and gluconic acid have been reported as unsatisfactory since only negligible amounts of nickel are deposited in their presence. The use of so-called "exaltants", i.e., certain anions such as soluble fluorides and those derived from short chain aliphatic dicarboxylic acids, has been found to increase the rate of nickel deposition even in the presence of chelating agents. However, there remains an unfulfilled need for an improved electroless nickel plating bath containing a complexing or chelating agent which will effectively prevent or minimize nickel phosphite precipitation without significantly affecting the rate of nickel deposition or materially lessening the life of the bath.

It is an object of the invention, therefore, to provide an improved electroless nickel plating bath which, in use, substantially reduces the problem of nickel phosphite formation and precipitation; to provide such a bath which is stable and may be used for a prolonged period without decomposing or breaking down; and to provide a bath of this type which permits a satisfactory rate of nickel plating and which produces nickel plating of good quality.

The present invention provides a bath for use in electroless nickel plating comprising an aqueous solution of a nickel salt, and a hypophosphite, characterised in that a glutamic acid compound selected from the group consisting of glutamic acid and the water soluble salts thereof is added to said bath. The invention also provides such a bath in dry, dehydrated form adapted for activation upon the addition of water to form an aqueous solution of the same components. The invention further provides a process of chemically plating nickel onto the surface of a substrate by contacting the substrate with an aqueous bath of the stated composition.

In accordance with the present invention, it has now been found that effective control of the formation and precipitation of nickel phosphite in electroless nickel plating may be achieved through the use of a bath comprising an aqueous solution of a water soluble nickel salt, a water soluble hypophosphite and glutamic acid or a water soluble salt thereof. It has been found that glutamic acid and its water soluble salts are highly effective chelating or complexing agents in electroless nickel plating baths and impart superior stability without deleteriously affecting the rate of nickel deposition. Baths containing glutamic acid or a water soluble glutamic acid salt prevent or substantially minimize the formation and precipitation of nickel phosphite and may be operated for more extended periods of time than available prior art baths without decomposition.

A preferred embodiment comprises an improved bath for use in electroless nickel plating constituted by an aqueous solution containing a nickel salt such as nickel sulfate hexahydrate, a hypophosphite such as sodium hypophosphite monohydrate and a glutamic acid compound such as monosodium glutamate monohydrate. The glutamic acid compound effectively functions as a chelating or complexing agent and minimizes the formation and precipitation of nickel phosphite. The bath can also optionally contain succinic acid or a soluble succinate salt and/or amonium or an alkali metal thiocyanate as exaltants or agents to accelerate the plating rate of the bath. For optimum results, the bath should contain a concentration of nickel ions within the range 0.079 to 0.189 mole/liter, a concentration of hypophosphite ions within the range 0.132 to 0.297 mole/liter and a concentration of glutamate ions at least twice that of the nickel ions. When included in the bath, the concentration of succinate ions is preferably at least twice that of the nickel ions and the amount of ammonium thiocyanate is between 0.3 and 0.6 parts per million. In plating with the bath, a temperature of 170°F. up to the boiling point of the bath, preferably 170—185°F., is employed and a pH of 4.0 to 9.0, preferably 4.5—4.7, is maintained.

Glutamic acid is any of its water soluble salts can be utilized to provide a source of glutamate ions in the bath. Thus, monoammonium glutamate, alkali metal salts of glutamic acid, such as monosodium glutamate and monopotassium glutamate, and alkaline earth metal salts of glutamic acid, such as calcium glutamate, can be used. The use of monosodium glutamate monohydrate is preferred since this compound is readily available and economical for use in electroless nickel plating.

The water soluble nickel salt employed can be any of various nickel salts known to the art such as nickel sulfate hexahydrate, nickel chloride, nickel bromide or nickel acetate. Similarly, various water soluble hypophosphites known to the art can be used, among which may be mentioned sodium hypophosphite, lithium hypophosphite, barium hypophosphite and magnesium hypophosphite.

For best results, it is preferred that the concentration of nickel ions in the bath be within the range 0.079 to 0.189 mole/liter, the concentration of hypophosphite ions within the range 0.132 to 0.297 mole/liter and that the concentration of glutamate ions be at least twice that of the nickel ions. Optimum results are realized when the ratio of hypophosphite ions to nickel ions in the bath is approximately 0.6 (on a molar basis), but it will be understood that higher or lower ratios may be used with satisfactory results. Further, best results are obtained when the nickel ion concentration is maintained at approximately 0.119 mole/liter and preferably between 0.0935 and 0.153 mole/liter.

In carrying out chemical plating of nickel onto a substrate, the bath should be maintained at a pH between 4.0 and 9.0. For optimum results, it is preferred to maintain the pH of the bath fairly constant at approximately 4.5—4.7. For the purpose of adjusting the pH during continuous plating operation with the bath, acids such as sulfuric acid and alkaline materials such as ammonium hydroxide, sodium carbonate, for example can be used.

Preferably, during plating ,the temperature of the bath is maintained between 175° and 185°F. However, if desired, the temperature can be varied within the range 170°F. up to the approximate boiling point of the bath. The higher temperatures within this range are less desirable since the bath then tends to decompose more readily.

While the formation and precipitation of nickel phosphite is substantially reduced and a satisfactory rate of plating is achieved with a bath containing only a soluble nickel salt, a soluble hypophosphite and a soluble glutamic acid compound, the plating rate may be enhanced by the addition of succinic acid or a water soluble succinate salt. The succinic acid or succinate salt functions as an "exaltant" and increases the rate of nickel deposition by activating the hypophosphite ions. Where a source of succinate ions is included, it is preferred that the concentration of succinate ions be at least twice that of the nickel ions.

Another exaltant material which may be optionally included either together with a source of succinate ions or in lieu thereof is a thiocyanate such as ammonium thiocyanate or an alkali metal thiocyanate such as sodium thiocyanate or potassium thiocyanate. The use of ammonium thiocyanate is preferred and, when incorporated into the bath, its concentration should be maintained between 0.3 and 0.6 parts per million, preferably 0.45 parts per million. For example, at concentration of 0.45 parts per million, it results in a two-fold increase in the plating rate. However, at concentrations below about 0.3 parts per million, ammonium thiocyanate exerts little or no exaltant effect and at concentrations above about 0.6 parts per million, it inhibits plating. The use of sodium thiocyanate or potassium thiocyanate is less preferable since these compounds tend to inhibit plating after several additions thereof during replenishment of the bath. On the other hand, the concentration of ammonium thiocyanate does not appear to build up in the bath even upon addition of further amounts during replenishment of the bath as described hereinafter.

Other optional components known to those skilled in the art may also be included if desired. For example, a stabilizer such as thiourea may be incorporated to assist in preventing decomposition of the bath and a wetting agent such as certain sulfonated materials may be incorporated to promote wetting of the parts to be plated by the bath.

The substrate or article to be nickel plated is normally prepared in accordance with conventional procedures such as those used in connection with electroplating processes, i.e., mechanical cleaning, degreasing, pickling, for example. Any catalytic material known to the art as operable in electroless nickel plating may be plated. Examples of such materials include copper, iron, cobalt, nickel, palladium, platinum, silver, gold, aluminum, boron, for example. The article or substrate to be plated can also be composed of a plastic material having a surface coating or film of an activated or catalytic material such as palladium.

For plating, the substrate or article is immersed in a suitable volume of the bath contained in a suitable receptacle such as a corrosion resistant steel tank lined with polypropylene and equipped with a steam or hot water jacket to supply the desired heat to the bath. The initial bath contains an amount of a suitable nickel salt necessary to supply a concentration of nickel ions within the ranges previously stated, an amount of a soluble hypophosphite necessary to supply a concentration of hypophosphite ions within the range given above and an amount of glutamic acid or a soluble glutamic acid salt necessary to supply a concentration of glutamate ions at least twice that of the nickel ions. The pH of the bath is adjusted to approximately 4.5—4.7 by the addition of appropriate quantities of a suitable alkaline material such as a 1:1 mixture of water and a 28% ammonium hydroxide solution and the bath is heated to the desired temperature, for example 175° F. As plating is initiated ,the evolution or bubbling of hydrogen gas will be observed.

As plating proceeds and nickel is deposited onto the activated substrate, the nickel in the bath becomes deplated and therefore must be replenished from time to time to maintain the concentration of nickel ions at the desired level within the range above stated and preferably at a level of approximately 0.102 to 0.118 mole/liter (6.0—7.0 g./liter). This is accomplished through the addition of a replenisher solution which may contain, for example, 150 g./liter of nickel sulfate hexahydrate or other soluble nickel salt and 105 g./liter of monosodium glutamate monohydrate or other soluble glutamate. Preferably, the pH of the replenisher solution is adjusted to be on the order of 6.5 to 7.0 by the addition of an alkaline material such as the above referred to mixture of ammonium hydroxide and water. During plating, the hydrogen ion concentration in the bath tends to increase. This hydrogen ion buildup is counteracted by the relatively high pH of the replenisher solution so that the pH of the bath can be maintained at the desired 4.5—4.7 level. The pH of the bath can also be independently adjusted during the plating operation as for example by the addition of an alkaline material when the bath becomes too acid as the nickel is depleted or by the addition of an acid such as a 1:2 mixture of water and concentrated sulfuric acid when the pH of the bath rises above the desired level.

The nickel ion concentration of the bath is determined by conventional methods known to the art at periodic intervals as plating proceeds, and the replenisher formulation is added to the bath as required along with an additional amount of a hypophosphite solution such as a sodium hypophosphite solution which, as previously mentioned, functions to reduce the nickel ions. Preferably, for example, the hypophosphite solution contains 570 g./liter of sodium hypophosphite. Preferably, one part of such a hypophosphite solution is mixed with six parts of the above noted replenisher solution and the resultant mixture, containing 29.0 g./liter of nickel (0.493 mole/liter) and 80.0 g./liter of sodium hypophosphite, is then added to the bath. As additions of the replenisher and hypophosphite mixture are made to replace nickel ions and hypophosphite ions depleted during the plating operation, the concentration of glutamate ions continues to build up without, however, affecting or decreasing the plating rate. In addition to effectively controlling the formation and precipitation of nickel phosphite, the glutamate ions also prevent the precipitation of nickel succinate which would otherwise tend to occur when succinate ions are included in the bath.

In practice, it has been found that the baths and process of the present embodiments significantly reduce nickel phosphite formation and precipitation, provide a significant increase in the stability and life of the baths and produce nickel platings of good brightness, adherence and ductility. As to bath life, it has been found that the baths may be replenished from 15—20 times (i.e., operated for 15—20 cycles) without decomposing or breaking down whereas available prior art baths generally decompose after only about 7—8 replenishments.

The baths can also be formulated in a dry or dehydrated form capable of being reconstituted or reactivated to form an aqueous bath upon the addition of a suitable volume of water. For this purpose, an aqueous bath is first formed containing a soluble nickel salt, a soluble hypophosphite and a soluble source of glutamate ions together with any desired optional component from among those previously described. The aqueous bath is then dehydrated, as by conventional spray drying at a temperature not in excess of 100°C., to produce the bath in powder form. If desired, the powder may then be pressed into pills or pellets or packaged in water-soluble plastic bags, each of these forms containing the desired quantities of the components of the bath. Upon dissolution in a predetermined volume of water, an aqueous bath containing the desired concentration of components is thus obtained in an easy and convenient manner preparatory to plating. Alternately the ingredients can be initially mixed in dry form and the bath can be constituted by addition of water to the mixture followed by adjustment of the pH of the bath.

The following examples illustrate the invention:

EXAMPLE 1

An aqueous bath formulation was prepared having the following composition:

Component	Amount
Nickel sulfate hexahydrate	31.6 g./liter
Monosodium glutamate monohydrate	60.0 g./liter
Sodium hypophosphite monohydrate	21.0 g./liter

The bath thus contained 0.119 mole/liter of nickel ions, 0.321 mole/liter of glutamate ions and 0.198 mole/liter of hypophosphite ions. The pH of the bath was adjusted to 4.6 by the addition of a 1:1 mixture of ammonium hydroxide (28% solution) and water.

A sample of mild steel was immersed in the bath which was maintained at a temperature of 175°F. It was found that nickel was plated onto the steel at the rate of 0.35 mil/hour.

From time to time, as required, the bath was replenished by the addition of a mixture of six parts of a solution containing 150 g./liter of nickel sulfate hexahydrate and 105 g./liter of monosodium glutamate hexahydrate (the solution having a pH of approximately 6.8) and one part of a solution containing 570 g./liter of sodium hypophosphite monohydrate. Periodic additions of this replenisher solution maintained the nickel ion concentration of the bath at approximately 0.119 mole/liter.

It was found that the bath could be operated for at least 15 cycles (15 replacements of the original nickel concentration via the replenisher solution) before decomposing.

EXAMPLE 2

An aqueous bath formulation was prepared having the following composition:

Component	Amount
Nickel sulfate hexahydrate	31.6 g./liter
Monosodium glutamate monohydrate	60.0 g./liter
Sodium hypophosphite monohydrate	21.0 g./liter
Succinic acid	30.0 g./liter
Ammonium thiocyanate	0.120 g./liter

The bath thus contained 0.119 mole/liter of nickel ions, 0.321 mole/liter of glutamate ions, 0.198 mole/liter of hypophosphite ions, 0.252 mole/liter of succinate ions and 0.45 parts per million of ammonium thiocyanate. The pH of the bath was adjusted to 4.6 as in Example 1.

The plating procedure of Example 1 was followed, the batch being maintained at a temperature of 175°F. and a pH of approximately 4.6. Periodic additions of the replenisher solution of Example 1 were made as required to maintain the nickel ion concentration of the bath at approximately 0.119 mole/liter.

It was found that nickel was plated onto the steel at the rate of 0.6 mil/hour and that the bath could be operated for 20 cycles before decomposing. The plating was of good quality as to brightness, adherence and ductility.

EXAMPLE 3

Example 2 was repeated except that the bath was maintained at a pH of 7.0 during plating. This increased the plating rate to approximately 1.0 mil/hour.

EXAMPLE 4

Example 2 was repeated except that the bath was maintained at a pH of 9.0 during plating . This increased the plating rate to approximately 1.5 mil/hour.

EXAMPLE 5

Example 2 was repeated except that the bath was maintained at a temperature of 185°F. and at a pH of 4.6. The plating rate was found to be 0.75 mil/hour.

The conditions employed in Example 2 are preferred insofar as the quality of the plating as to brightness, adherence and ductility is concerned, although the conditions employed in the other examples give platings of satisfactory quality.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

Various changes can be made in the above illustrative embodiments without departing from the scope of the invention as defined in the appended claims.

WHAT WE CLAIM IS:—

1. A bath for use in electroless nickel plating comprising an aqueous solution of a nickel salt and a hypophosphite, characterized in that a glutamic acid compound selected from the group consisting of glutamic acid and the water soluble salts thereof is added to said bath.

2. A bath for use in electroless nickel plating as set forth in claim 1 further characterized in that the nickel salt is nickel sulfate hexahydrate, the hypophosphite is sodium hypophosphite monohydrate and the glutamic acid compound is monosodium glutamate monohydrate.

3. A bath for use in electroless nickel plating as set forth in claim 1 or claim 2 further characterized in that the bath additionally contains a source of succinate ions.

4. A bath for use in electroless nickel plating as set forth in any one of the preceeding claims further characterized in that the bath additionally contains ammonium thiocyanate.

5. A bath for use in electroless nickel plating comprising an aqueous solution of a nickel salt and a hypophosphite, characterized in that the bath additionally contains a glutamic acid compound selected from the group consisting of glutamic acid and the water soluble salts thereof, the concentration of nickel ions being within the range 0.079 to 0.189 mole/liter, the concentration of hypophosphite ions being within the range 0.132 to 0.297 mole/liter and the concentration of the glutamate ions being at least twice that of the nickel ions.

6. A bath for use in electroless nickel plating as set forth in claim 5 further characterized in that the pH of said bath is within the range 4.0 to 9.0.

7. A bath for use in electroless nickel plating as set forth in claim 5 or claim 6 further characterized in that the ratio of

hypophosphite ions to nickel ions on a molar basis is approximately 0.6.

8. A bath for use in electroless nickel plating as set forth in any of claims 5, 6 or 7 further characterized in that the bath additionally contains a source of succinate ions, the concentration of succinate ions being at least twice that of the nickel ions.

9. A bath for use in electroless nickel plating as set forth in any one of claims 5, 6, 7, or 8 further characterized in that the bath additionally contains between 0.3 and 0.6 parts per million of ammonium thiocyanate.

10. A water soluble composition for preparing an aqueous bath for use in electroless nickel plating comprising a water soluble nickel salt and a water soluble hypophosphite, characterized in that the composition additionally contains a glutamic acid compound selected from the group consisting of glutamic acid and the water soluble salts thereof.

11. A water soluble composition for preparing an aqueous bath for use in electroless nickel plating as set forth in claim 10 or claim 11 further characterized in that the nickel salt is nickel sulfate hexahydrate, the hypophosphite is sodium hypophosphite monohydrate and the glutamic acid compound is monosodium glutamate monohydrate.

12. A water soluble composition for preparing an aqueous bath for use in electroless nickel plating as set forth in any one of claims 10, 11 or 12 further characterized in that the composition additionally contains a material selected from the group consisting of a source of succinate ions and ammonium thiocyanate.

13. A water soluble composition for preparing an aqueous bath for use in electroless nickel plating comprising a water soluble nickel salt and a water soluble hypophosphite, characterized in that the composition additionally contains a glutamic acid compound selected from the group consisting of glutamic acid and the water soluble salts thereof, the composition upon being dissolved in a predetermined volume of water producing an aqueous solution containing a concentration of between 0.079 and 0.189 mole/liter of nickel ions, a concentration of between 0.132 and 0.297 mole/liter of hypophosphite ions and a concentration of glutamate ions at least twice that of the nickel ions.

14. A water soluble composition for preparing an aqueous bath for use in electroless nickel plating as set forth in claim 13 further characterized in that the ratio of hypophosphite ions to nickel ions in said aqueous solution is approximately 0.6 on a molar basis.

15. A water soluble composition for preparing an aqueous bath for use in electroless nickel plating as set forth in claim 13 or claim 14 further characterized in that the composition additionally contains a source of succinate ions, the concentration of succinate ions in said aqueous solution being at least twice that of the nickel ions.

16. A water soluble composition for preparing an aqueous bath for use in electroless nickel plating as set forth in any one of claims 13, 14 or 15 further characterized in that the composition additionally contains ammonium thiocyanate and said aqueous solution contains between 0.3 and 0.6 parts per million of ammonium thiocyanate.

17. A process of chemically plating nickel onto the surface of a substrate which comprises contacting said substrate with a bath comprising an aqueous solution of a nickel salt and a hypophosphite characterized in that said bath additionally contains a glutamic acid compound selected from the group consisting of glutamic acid and the water soluble salts thereof.

18. A process of chemically plating nickel onto the surface of a substrate as set forth in claim 17 further characterized in that the nickel salt is nickel sulfate hexahydrate, the hypophosphite is sodium hypophosphite monohydrate and the glutamic acid compound is monosodium glutamate monohydrate.

19. A process of chemically plating nickel onto the surface of a substrate as set forth in claim 17 or claim 18 further characterized in that the bath additionally contains a source of succinate ions.

20. A process of chemically plating nickel onto the surface of a substrate as set forth in any one of claims 17, 18 or 19 further characterized in that the bath additionally contains ammonium thiocyanate.

21. A process of chemically plating nickel onto the surface of a substrate which comprises contacting said substrate with a bath comprising an aqueous solution of a nickel salt and a hypophosphite characterized in that the bath additionally contains a glutamic acid compound selected from the group consisting of glutamic acid and the water soluble salts thereof, the concentration of nickel ions being within the range 0.079 to 0.189 mole/liter, the concentration of hypophosphite ions being within the range 0.132 to 0.297 mole/liter and the concentration of glutamate ions being at least twice that of the nickel ions.

22. A process of chemically plating nickel onto the surface of a substrate as set forth in claim 21 further characterized in that the pH of said bath is within the range 4.0 to 9.0.

23. A process of chemically plating nickel onto the surface of a substrate as set forth in claim 21 or claim 22 further charac-

terized in that the ratio of hypophosphite ions to nickel ions on a molar basis is approximately 0.6.

24. A process of chemically plating nickel onto the surface of a substrate as set forth in any one of claims 21, 22 or 23 further characterized in that the bath additionally contains a source of succinate ions, the concentration of succinate ions being at least twice that of the nickel ions.

25. A process of chemically plating nickel onto the surface of a substrate as set forth in any one of claims 21, 22, 23 or 24 further characterized in that the bath additionally contains between 0.3 and 0.6 parts per million of ammonium thiocyanate.

26. A process of chemically plating nickel onto the surface of a substrate, the process being substantially as described herein with reference to any of Examples 1 to 5.

27. A substrate chemically plated with nickel by a process as set forth in any of claims 17 to 26.

28. A bath for use in electroless nickel plating, the bath being substantially as described herein with reference to any of Examples 1 to 5.

29. A water soluble composition for preparing an aqueous bath for use in electroless nickel plating, the composition being substantially as described herein with reference to Example 1 or 2.

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